CHROMIUM

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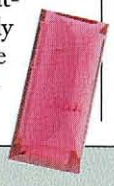
I WAS DESTINED TO WORK ON CHROMIUM: My mother's name was Ruby. Mom loved the stunning red gemstone, but she didn't know there would be a ruby laser, and neither did I, during the late 1940s and early '50s when I was experimenting with chromium compounds in the basement of our house. I had quite a nice lab, and I remember that Mom was worried that I would blow myself up, especially when I used dichromate as an oxidant in spectacularly exothermic redox reactions.

PHOTODISC

SEEING RED **Chromium impurities in corundum give rubies their distinctive red color.**

In college, I worked on the analytical chemistry of chromium and three of its neighbors: vanadium, niobium, and molybdenum. Although I loved the challenge of analyses, the inorganic research that Fred Basolo and Ralph Pearson were doing at Northwestern University excited me even more, and I joined their group in 1958. The late '50s were the glory days of inorganic mechanisms, and chromium was one of the big stars. The chromous ion, which is a powerful reductant and can attack oxidants at close range, is substitution labile; and, as all inorganic chemists know, the chromium product of the reaction, Cr(III), is substitution inert. Henry Taube's famous experiment demonstrating atom transfer from chloropentaamminecobalt(III) to chromous ion relied on these properties of two of the more common oxidation states of the element.

In my work in Copenhagen in the spring of 1961, I became fascinated with oxo complexes, especially the vanadyl and chromyl ions. The garnet-red ammonium pentachlorooxochromate(V) contains the triply bonded oxochromium(V) unit, and Curtis R. Hare and I interpreted its d-d spectrum [*Inorg. Chem.*, **1**, 363 (1962)]. (Later, with Carl J. Ballhausen and V. M. Miskowski, I worked on the spectra of chromate and halochromates, which, like dichromate, are all in the VI oxidation state made famous by Julia Roberts in the movie "Erin Brockovich.")



During the next year at Columbia University, Nancy Beach and I worked on zerovalent chromium: We reported that the UV spectrum of its carbon monoxide complex, chromium hexacarbonyl, exhibits two very intense absorptions that are attributable to metal-to-ligand charge-transfer (MLCT) transitions. Amazingly, our interpretation of the hexacarbonyl MLCT spectrum has withstood 40 years of theoretical scrutiny, although the positions of the lowest d-d excitations have been revised by density functional theorists. The excited-state dynamics of the molecule are now understood in great detail, and for that reason, zerovalent chromium usually makes an appearance in textbooks that have sections on the photochemistry of metal complexes.

The chromous ion is very special to me, as it launched my work on electron tunneling through proteins. In the early '70s, colleagues and I used aqueous Cr(II) to transfer electrons to the blue copper centers in spinach plastocyanin, bean plastocyanin, *Rhus vernicifera* laccase, and stellacyanin [*Proc. Natl. Acad. Sci. USA*, **69**, 30 (1972)]. Our experiments showed that electron transfers to some copper centers were much slower than others, and we now know that in most biological reactions electrons must tunnel through many bonds to reach their destinations. Much later, in work reminiscent of Taube's, Israel Pecht and Ole Farver identified one of the Cr(III)-protein binding sites after Cr(II) reduction. In so doing, they estimated how far an electron had to travel in its journey to a copper active site.

Many investigators have explored the spectroscopy and chemistry of the d-d excited states of octahedral Cr(III), and the excited doublet, in particular, has had a long and glorious (some say checkered) history. Whether the doublet undergoes associative substitution is still debated when "inorganikers" gather for discussions of mechanisms. In 1985, with Bruce S. Brunschwig and other colleagues, we examined the rates of oxidation of reduced blue-copper proteins by this relatively long-lived and powerfully oxidizing Cr(III) reagent, in one of the early demonstrations of electron tunneling through folded polypeptides [*Inorg. Chem.*, **24**, 3743 (1985)].

All in all, I have worked on six oxidation states of chromium. In recent times, and in collaboration with Zeev Gross of Technion-Israel Institute of Technology, our group has managed to prepare chromium corroles in four oxidation states, III through VI, although "VI" turned out to be V complexed to an oxidized corrole. The joint Technion-California Institute of Technology research on aerobic oxidations catalyzed by chromium corroles is the latest chapter in my affair with element 24.

Harry B. Gray *is the Arnold O. Beckman Professor of Chemistry at Caltech. He received the National Medal of Science in 1986 and the Priestley Medal in 1991; in 2003, he received the Nichols and Wheland Medals as well as the National Academy of Sciences Award in Chemical Sciences.*

Cr
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CELEBRATING C&EN'S 80TH ANNIVERSARY

CHROMIUM AT A GLANCE

Name: From the Greek *chroma*, color.

Atomic mass: 52.00.

History: Discovered in 1780 by Nicholas Louis Vauquelin.

Occurrence: Isolated mostly from chromite ore.

Appearance: Blue white, hard and brittle metal.

Behavior: Resists oxidation in air. Many chromium compounds are toxic. Chromates are corrosive to skin and tissue. Chromium itself is a human poison if ingested and is suspected of being a carcinogen. The presence of chromium impurities in gems is often responsible for their brilliant colors.

Uses: Essential trace element in humans that plays a role in glucose metabolism. In alloys, chromium can serve as a protective coating from oxidation and comprises up to 18% of stainless steel. Its oxides are often used as pigments, for tanning leather, and in high-quality recording tapes.